

The University of Chicago

ADSORPTION ON PLATINUM OF
HYDROCHLORIC ACID FROM
AQUEOUS SOLUTION

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1935

By
PAUL JACKSON HARTSUCH

CHICAGO, ILLINOIS

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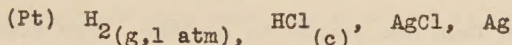
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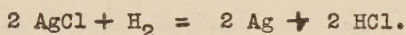


INTRODUCTION

When Anderson¹ was studying the cell:



he found that in very dilute hydrochloric acid solutions the following reaction occurred slowly at the surface of the platinized electrode:



As a consequence of this reaction, the concentration of hydrochloric acid increased slowly and it was necessary to determine it accurately after the final e.m.f. measurement. The solutions were too dilute to be analyzed by precipitation of the chloride ion as silver chloride; consequently a conductimetric method of analysis was employed. Immediately after the final e.m.f. measurement the platinized electrode was removed to prevent further reduction of silver chloride. The resistances of samples of the solution were determined in a conductance cell by the usual Kohlrausch method. It was possible then to calculate the concentration of the solution from its resistance, and that of a calibrating solution. The latter consisted of a dilute hydrochloric acid solution of known concentration (approximately the same as the solution in the e.m.f. cell), which was prepared and stored in a three liter quartz flask. The resistance of this solution was determined in the same conductance cell.

In an attempt to extend the work of Anderson to other temperatures and higher concentrations, this same conductimetric

¹N. J. Anderson, Ph. D. Thesis, University of Chicago, 1934.

method of analysis was employed. Constant and reproducible values for the resistance of the calibrating solution in the conductivity cell were obtained with no trouble. However, the resistance of the dilute hydrochloric acid solution from the e.m.f. cell varied with time, and from one sample to another. For example, the resistance of one calibrating solution was 735.9 ohms. The apparent resistance of the solution from the e.m.f. cell varied from 757 ohms for one sample left in the conductivity cell nearly two hours, to 726-731 ohms for four samples, each of which was left in the cell for 25 to 30 minutes.

In another experiment, the resistance of the calibrating solution, about 0.0004 M HCl, was 1,282.3 ohms. The resistances of the solutions saturated with both hydrogen and silver chloride which were removed from the e.m.f. cell varied from 1,184 to 1,299 ohms. The resistance of most of the samples was lower than the resistance of the calibrating solution; one sample, left over night in the cell, yielded a resistance about seventeen ohms greater than that of the calibrating solution. Similar erratic results were obtained with two other solutions from the e.m.f. cell, one about 0.0004 M and the other about 0.0001 M in HCl.

Before the e.m.f. study could be continued, it was necessary to ascertain the cause of this erratic behavior. This problem proved to be so complex and interesting that the investigation was diverted and extended in this direction.

APPARATUS

The conductance apparatus was arranged as shown in Figure 1. A Leeds and Northrup type of Kohlrausch slide wire (No. 4258, Serial No. 73441) was employed. This slide wire is equipped with equal resistance end coils, Aa and Bb, and a drum type slide wire, ab. While it has been shown by Jones and Joseph¹ that absolute conductance values cannot be obtained with this type of slide wire, the error is not over 0.005 per cent if the point of balance is maintained between 480 and 520 on the slide wire. The point of balance was kept between 495 and 505 for all measurements in this work, except those of the 0.01 M HCl solutions. The resistance of these solutions was so low that a change of one ohm in the known resistance, changed the slide wire reading about 50 divisions.

The method of grounding the bridge was similar to that used by Jones and Joseph. Since the total resistance of the drum and end coils between A and B is approximately 70 ohms, resistance T was made approximately 70 ohms also. The method of operation of switch S, and slide wire g and resistance T, was the same as described by Jones and Joseph.

The known resistance, R, was a Leeds and Northrup five dial instrument (Serial No. 32299). It was calibrated by the method outlined by Anderson.² A Leeds and Northrup plug box (Serial No. 120642), with Curtis wound coils was used as the

¹Jones and Joseph, J. Am. Chem. Soc., 50, 1049 (1928).

²Anderson, op. cit., pp. 26-27.

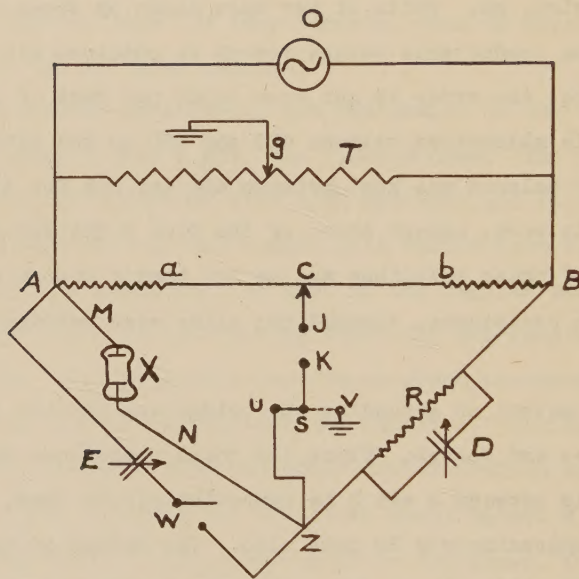


Fig. 1

auxiliary resistance instrument. The calibrations were not applied to any of the resistance values reported in this work, since they amounted to only 0.01 per cent or less of the total resistance in any measurement.

A twenty-one plate variable air condenser, D, with a maximum capacity of 400 micro-micro-farads, was placed in parallel with the known resistance R, to balance the capacity effects of the conductance cell, X. The adjustment of this condenser was often critical, especially with solutions of a high resistance. If it was not adjusted properly, there was no region of complete silence at the balance point.

The capacity of some of the conductance cells was less than the minimum capacity of condenser D. The capacities were balanced then by the closing of switch W; this introduced into the circuit in parallel with cell X, a 43 plate variable condenser E. A point of silence in the earphones was obtained then by a careful adjustment of condenser D.

Wires lead from J and K in Figure 1 to the input of a two stage audio frequency amplifier, constructed by Dr. N. J. Anderson. The earphones were inserted in the output circuit of this amplifier. The two "01-A" vacuum tubes were operated at their rated voltage of 5.0 volts, by a six volt lead storage battery. A plate potential of 90 volts and a negative grid bias of 4.5 volts were used. These are customary values.¹ A metal shield was placed inside of the amplifier box and grounded, to prevent the formation of an induced current in the audio frequency transformers, from the operation of a nearby alternating current motor. No sixty cycle note could be heard in the phones, and it was possible to make accurate

¹"RCA Radiotron-Cunningham Radio Tube Manual," Technical Series RC-11.

conductance measurements while the thermostat motor was running. A vacuum tube amplifier such as this one increases the sensitivity of conductance measurements and they have been used in most recent conductance work. An attempt was made to substitute a commercial "B eliminator" for the two 45 volt B batteries. The sixty cycle hum from the eliminator could be heard in the phones, and interfered with the determination of the balance point.

The vacuum tube oscillator, O, was constructed according to the directions given by Jones and Joseph.¹ At first an "01-A" tube was used to produce oscillations; later it was replaced with the newer "30" tube. A commercial "B eliminator" was used to supply the positive plate potential. No sixty cycle note could be heard in the phones. The oscillator was placed fifteen feet from the bridge to prevent magnetic coupling. Grounded lead covered wires were used to connect the oscillator with the bridge.

To make a conductance reading, the conductance cell was filled with the desired solution, and immersed in the oil of the thermostat. The thermostat was adjusted so that a reading of 3.995 ± 0.005 degrees on a Beckmann thermometer was maintained. The reading indicated a temperature within a few hundredths of a degree from 25°C. Two U shaped tubes of Pyrex glass, filled with mercury, were immersed in the thermostat oil and were carefully insulated from each other. Heavy copper wires of a U shape were used to complete the electrical circuit between the mercury in the U tubes and the mercury in the side arms of the conductance cell. Connection was made to the bridge by two heavy copper wires, M and N (Figure 1), which dipped into the other arm of the U tubes.

After the solution in the cell had attained a constant temperature, the resistance was measured as follows: the filament

¹Loc. cit.

voltage on the amplifier tubes was adjusted to five volts, by the use of a variable filament rheostat. Then a switch was closed to supply the alternating current for the "B eliminator" of the oscillator. Another switch was closed, which allowed current to pass through the filament of the oscillator tube. A note was heard then in the phones. Resistance R was adjusted so that the minimum came as near to the center of the slide wire, ab, as possible. Condenser D was adjusted to give a minimum note. A final adjustment of the slide wire, ab, was made then to produce silence in the earphones.

When the resistance was known approximately, the above steps could be completed in less than one minute, often in ten seconds. If a series of measurements was being made over a short period of time, the switch in the "B eliminator" circuit was left closed. The oscillator switch was opened after each measurement, since it is claimed that after a time the passage of the alternating current through the cell solution warms it slightly. The slide wire, g, on the resistance T, was not adjusted for each reading, as it was found that this was not necessary.

Four conductance cells were used for most of the resistance measurements described in this research. These cells are illustrated in Figure 2.

The soft glass cell, A, was employed to manufacture hydrochloric acid solutions of higher or lower resistance than the standard value. This was accomplished, as will be described in detail later, by the bubbling of different gases into the solution in the cell through the side arm, a. This cell was equipped with a ground glass stopper, b. The maximum capacity of the cell was about 50 cc. but most of the experiments were per-

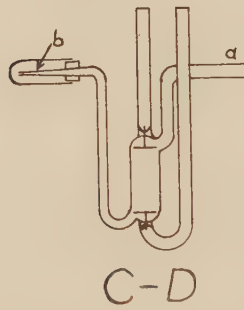
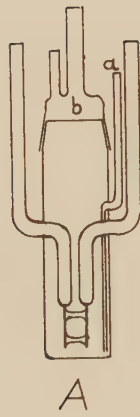


Figure 2

formed with 35.00 cc., measured from a burette, or 39.80 cc. of solution, which was three times the volume contained in a quartz pipette. The electrodes were approximately 2 x 2 cm. and were about 1 cm. apart.

The quartz cell, B, was used in several of the earlier experiments. It had a capacity of 26.5 cc., twice the volume contained in the quartz pipette. The electrodes were attached to the ground glass stopper. They were approximately 1.4 x 1.5 cm., and were about 1.2 cm. apart. The difficulty experienced with this cell was in the reproducing of the orientation of the ground glass stopper. If it was not placed in exactly the same position each time, the distance between the top of the electrodes and the surface of the liquid would not be exactly the same, and this condition would alter the resistance somewhat. In general, it was much easier to obtain constant and reproducible values with cell A than with this quartz cell.

Two cells, C and D, of the Washburn¹ type were employed. Both were of Pyrex glass. They were filled nearly to the top of each side arm with the solution to be measured, and consequently a small change in the volume of liquid in the cell made no appreciable change in the observed resistance. The electrodes of cell C were platinized, while those of cell D were of new, bright platinum. The capacity of cell C was about 5.6 cc. The circular electrodes were approximately 1.3 cm. in diameter, and were about 2.4 cm. apart.

The solution to be introduced into cells C and D was poured into a 20 cc. glass stoppered weighing bottle. A rubber tube was attached to side arm, a, and tip, b, was immersed in the solution, some of which was drawn into the cell by suction through

¹Washburn, J. Am. Chem. Soc., 38, 2431 (1916).

the rubber tube. The tip, b, was then protected with a glass cup, which fit over the tip without touching it. The side arm, a, was closed with a one inch length of rubber tubing, which contained a glass bead.

A long U-shaped conductance cell with old platinized electrodes was used for the analysis of 0.1 M HCl solutions, the resistances of which were too low for measurements in the cells previously mentioned. This U-shaped cell has been described by Urbane.¹

¹W. M. Urbane, Ph.D. Thesis, University of Chicago, 1934, p. 11.

MATERIALS

The stock solution of hydrochloric acid was prepared in a manner similar to that described by H. C. Parker.¹ The actual apparatus was the same as that used by Anderson.² The hydrogen chloride evolution was controlled by the addition of approximately one drop per minute of J. T. Baker's "Analyzed" sulfuric acid, to the dry sodium chloride in the generating flask. The sodium chloride was also a J. T. Baker "Analyzed" product. The generating flask was never heated.

The hydrogen chloride gas, dried by passage through concentrated H_2SO_4 and P_2O_5 , was absorbed in a weighed quantity of water in a 500 cc. fused quartz flask. The approximate molality was determined by the increase in weight of the flask and contents due to the hydrochloric acid absorbed. The actual molality was determined gravimetrically by silver chloride precipitation in a manner similar to that described by Richards³ and his co-workers, except for certain refinements which were necessary in the atomic weight work which they were doing, but which were not deemed necessary for the precision desired in this work.

A sample of the hydrochloric acid solution large enough to

¹Parker, J. Am. Chem. Soc., 45, 2017 (1923).

²Anderson, op. cit., p. 28.

³Richards and Willard, Carnegie Inst. Pub., No. 125 (1910); Richards and Staehler, J. Am. Chem. Soc., 29, 632 (1907); Richards and Staehler, Carnegie Inst. Pub., No. 69 (1907); Richards and Wells, Carnegie Inst. Pub., No. 28 (1905).

give a final weight of silver chloride between 1.2 and 1.3 gm. was weighed carefully. It was transferred quantitatively with conductivity water to a 250 cc. beaker, which contained five cubic centimeters of 0.1 N HNO_3 . The total volume was adjusted to about 150 cc. with conductivity water. Since the approximate molality of the hydrochloric acid solution was known, the amount of 0.1 N AgNO_3 solution required to react with the weighed quantity of hydrochloric acid solution was calculated. This volume of silver nitrate solution was added dropwise, with constant stirring, in an electrically lighted room. Under these conditions the silver nitrate remained white. It is important that the silver nitrate solution be added dropwise, with stirring, and that there be but a slight excess at the end, to avoid occlusion of silver nitrate in the silver chloride precipitate.

The beaker was covered with a watch glass and left over night in a dark place. The next morning the precipitate had coagulated. A few drops of silver nitrate solution were added to test the completeness of precipitation. If the solution became cloudy, 0.5-1.0 cc. of silver nitrate solution was added and the solution left until the next day.

Between 1.5 and 2.0 cc. of 0.1 N AgNO_3 solution in excess of that required for complete precipitation was added before the precipitate was filtered, and the solution was allowed to stand for three or four hours, to secure the slight increase in the silver chloride precipitate due to the common ion effect.

The precipitate was washed about seven times by decantation with ice cold 0.01 N HNO_3 . Conductivity water was used to make this solution. About 25 cc. was used for each washing. The decanted liquid was poured through a Jena sintered glass filter, previously carefully weighed. The precipitate was then washed onto the filter

with small portions of the 0.01 N HNO_3 solution. The stirring rod and sides of the beaker were cleaned with a rubber policeman and the small amount of precipitate thus freed was rinsed onto the filter with the HNO_3 solution.

The precipitate on the filter was washed twice only with ice cold conductivity water. The precipitate was drained by suction as dry as possible. The porous glass filter with the precipitate was then transferred to a small beaker. The beaker was covered with a watch glass and placed in an electrically heated oven at 135-150°C. for four hours or more. It was then removed. The filter was placed in a desiccator to cool, and was then weighed. A glass counterpoise of approximately the same size and weight as the sintered glass filter was used. All weights were corrected for air buoyancy. In the calculation of the molality of the hydrochloric acid solution, the value 0.25440 was used for the ratio HCl/AgCl , and the molecular weight of HCl was taken as 36.454.

Parker claimed that he had ascertained the strength of his hydrochloric acid solutions "within a few thousandths of one per cent" from the increase in weight of the flask and contents due to the hydrogen chloride absorbed. It was not possible to check his results. The silver chloride precipitation method gave molalities from one to nearly five per cent greater than the molality calculated from the increase in weight. This indicated that under the conditions employed not all of the hydrogen chloride was absorbed and that which escaped through the neck of the flask carried water vapor with it; the solution was thus more concentrated than was indicated by the increase in weight.

The weaker solutions used in the conductance measurements were made from these stronger analyzed hydrochloric acid solutions

by weight dilution with conductivity water.

The conductivity water was prepared by redistillation of the laboratory distilled water in a fifty gallon tinned copper still. The operation of this still has been described by Anderson.¹ The water was stored in four liter Pyrex bottles until used. These bottles were used only for conductivity water and had not been contaminated with cleaning solution for more than a year.

The tank oxygen used was manufactured by Gases, Inc., by the liquifaction of air, and was intended for medicinal use. According to Moser,² commercial oxygen contains only traces of nitrogen and carbon dioxide. Consequently, the only treatment given to it was to bubble it through four wash bottles each filled with glass beads and containing approximately the same hydrochloric acid solution as the one in the conductance cell.

The water pumped nitrogen used was manufactured by Air Reduction Sales Co. It was bubbled first through four Erlenmeyer flasks arranged as wash bottles and filled with glass beads and the same solution as that in the conductance cell. No attempt was made to remove any oxygen present in the nitrogen.

The hydrogen used in the first part of the work was produced by three U-shaped electrolytic generators connected in parallel, drawing two to three amperes from an eighteen volt D. C. line. The liberated hydrogen gas bubbled through concentrated sulphuric acid then passed over a heated platinum wire to remove, supposedly, traces of oxygen in the hydrogen. This method was suggested by Lewis, Brighton and Sebastian.³

¹Anderson, op. cit., pp.29-31.

²Moser, Z. anorg. allgem. Chem., 110, 125 (1920).

³Lewis, Brighton and Sebastian, J. Am. Chem. Soc., 39, 2245 (1917).

In the later experiments, electrolytic tank hydrogen, manufactured by Gases, Inc., was employed. It likewise was bubbled through four wash bottles, each of which contained the same solution as that in the conductance cell, before it was bubbled through the solution in the cell.

A number of tests¹ have been devised for the detection of traces of oxygen in other gases, principally nitrogen and hydrogen. In the method of Mugden and Sixt, a known volume of a colorless ammoniacal cuprous chloride solution reacts with the oxygen in a known volume of gas. The resulting blue color is compared with that of an ammoniacal cupric sulfate solution of known strength. The special apparatus which they described was built and used to test the purity of the tank hydrogen. The method was satisfactory and indicated about 0.08 per cent oxygen in the tank hydrogen gas.

¹Binder and Weinland, Ber., 46, 255 (1913); C. A., 7, 1459 (1913); C. Van Brunt, J. Am. Chem. Soc., 36, 1448 (1914); Kautsky and Thiele, Z. anorg. chem., 152, 342 (1926); Warburg and Kubowitz, Biochem. Z., 202, 387 (1928); C. A., 23, 3183 (1929); Lubberger-Wunsch method, Gas u. Wasserfach, 72, 525 (1929); C. A., 23, 4163 (1929); Hamon, Mayer and Plantefol, Ann. physiol. physico-chim. biol., 6, 452 (1930); C. A., 25, 4292 (1931); Mugden and Sixt, Z. angew. Chem., 46, 90 (1933).

EXPERIMENTAL RESULTS

Chemical Analyses of Abnormal Solutions

To arrive at an explanation for the increases and decreases in resistance in the conductance cells which had been observed with hydrochloric acid solutions containing dissolved gases, it was necessary to investigate any changes in the hydrogen ion and chloride ion concentrations of the solution. This could be accomplished by direct titration if sufficiently large abnormal effects could be obtained in sufficiently concentrated solutions.

The molality of the hydrochloric acid solutions studied previously varied from 0.0002 to 0.002. A 0.1 M solution was selected for investigation in cell A, the electrodes of which were replatinized. A platinum chloride solution was used which contained a trace of lead acetate. A current of thirty milliamperes was passed for eighty-four minutes, with a reversal of current every two to five minutes. The cell was washed, filled with water, and allowed to stand for several hours. After it had been rinsed several times with the 0.1 M hydrochloric acid solution, hydrogen was bubbled through a sample in the cell. The resistance of the solution was 0.28 per cent lower than standard, when it was determined in the U-shaped conductance cell. After a single rinsing, just enough solution (about one-third of the volume used previously) was introduced into cell A to cover the electrodes. Hydrogen was bubbled through this solution for an hour, after which time the resistance was approximately constant.

The resistance was found to be 0.77 per cent less than standard, when it was determined in the U-shaped cell. When the second low resistance solution was removed from the cell, it was replaced without rinsing with another sample of about the same volume. This was left over-night and then transferred to the U-shaped cell for analysis. Its resistance was 0.44 per cent greater than standard.

Only 10 cc. portions of these last two solutions were available for analysis. These were titrated for acidity, but no definite increase or decrease could be noticed, since the titration error was as great as the observed change in the resistance of the solutions from the standard resistance. Both of the low resistance solutions containing hydrogen gave positive tests for hydrogen peroxide, when the titanium sulfate was added. A concentration of approximately one part of hydrogen peroxide per 400,000 parts of solution was estimated.

A. M. Vasil'ev¹ claimed that a certain amount of platinum was dissolved when moist platinum black remained in contact with 2N hydrochloric acid "for some time." The oxygen of the air, he said, acted as the oxidizing agent, and chlorplatinic acid was the product.

The 0.1 M hydrochloric acid solution which had remained over-night in contact with the platinum black conductance electrodes was tested for Pt in solution, by the passing of hydrogen sulfide into the hot solution.² A decided darkening

¹A. M. Vasil'ev, Sci. Rept. State Univ. Kazan, 90, 989 (1930); C. A., 26, 5825 (1932).

²Treadwell and Hall, "Analytical Chemistry," Vol. 1, Qualitative Analysis, fourth English edition, John Wiley and Sons, Inc., New York, 1916, p. 84.

occurred. No darkening occurred in a control sample (0.1 M hydrochloric acid which had not been in the cell). The darkening might have been due to PtS_2 , but a test with hydrogen sulfide is not characteristic for platinum, of course. The precipitate might have been PbS from traces of lead acetate on the electrodes.

Since the per cent change in resistance of the 0.1 M solution was only 0.22 to 0.77 per cent, it was necessary to use a more dilute solution in which the effect would be larger, and yet one concentrated enough to make ordinary titration methods feasible. A 0.01 M solution was chosen for a comparison of the changes in conductivity and in total hydrogen ion and chloride ion concentration. Samples were placed in cell A, and hydrogen and oxygen were bubbled successively through them. Resistance measurements were made frequently during the bubbling; the last one of each sample just preceded the removal of a 25 cc. portion to a beaker. Two drops of a 0.04 per cent solution of methyl red were added, and the solution titrated with 0.01 M NaOH. Several drops of the NaOH solution were required to change the color of the indicator from red to yellow. Twenty-five cubic centimeters of the standard 0.01 M HCl solution from the three liter quartz flask was titrated with the same 0.01 N NaOH and the same amount of indicator solution, to an arbitrary end-point, between the red and yellow color. The solutions from the conductance cell were therefore titrated until a color match was obtained with the standard. The end-point could be estimated with a precision of one drop of NaOH solution. The per cent difference between the amount of 0.01 N NaOH required for the titration of each solution

and that required for the standard hydrochloric acid solution is in column five of Table VI. The difference in corresponding resistances appears in column four.

TABLE VI

Sample No.	Gas Bubbled	Time of Bubbling, Minutes	Per cent Decrease in Resistance	Per cent Increase in NaOH required
1	H ₂	36	2.36	2.13
2	H ₂	41	2.47	2.51
3	O ₂	34	-2.53	-2.59
4	H ₂	50	2.52	2.31
5	O ₂	34	-2.22	-2.54
6	O ₂	40	0.01	-0.23
7	N ₂	..		
8	N ₂	52	-0.04	
9a	O ₂	60	-0.04	
9b	H ₂	69	2.31	2.50 (Cl ⁻)
10	H ₂	57	0.07	
11	N ₂	57	-2.46	
12	N ₂	62	-0.02	
13	H ₂	77	2.27	
14	None	..	-1.48	-1.58
15	H ₂	61		3.77

After the standard resistance for the 0.01 M HCl had been determined, solution No. 1 was introduced into cell A and hydrogen was bubbled through it for thirty-six minutes; a constant low resistance was obtained before the bubbling was stopped. Between samples 1 and 2, the cell and electrodes were rinsed with a fresh portion of the 0.01 M HCl. Thereafter, the cell and electrodes were not rinsed between fillings. One solution (as No. 2) was removed, and the next solution (No. 3 in this case) was introduced at once. The exact routine employed is important, because it was found that the behavior of a solution when oxygen or hydrogen was bubbled through it in the conductivity cell, depended on the previous history of the cell electrodes.

The data in columns four and five of Table VI show that

the changes in the resistances are very closely correlated with the changes in total hydrogen ion concentration. It is obvious therefore that the changes in resistance are not due to large changes in the immediate neighborhood of the electrodes, or to some other spurious electrode effect. They correctly represent actual changes in acidity occurring throughout the body of the solution.

Similar changes in hydrogen ion concentration have been reported by several previous investigators. Frumkin and Donde¹ discovered that a neutral sodium sulfate solution, containing dissolved hydrogen, became acid when brought into contact with spongy platinum, due supposedly to an adsorption of alkali on the platinum. When oxygen was bubbled through another sample of a neutral sodium sulfate solution, the solution became alkaline.

Denham and Morris² noticed that the apparent pH of solutions of cadmium sulfate and zinc sulfate was less when measured with a hydrogen electrode than when a quinhydrone electrode was used. The solutions had become more acid in the presence of the platinized platinum surface and hydrogen gas.

Kolthoff and Kameda³ verified the results of Frumkin and Donde, and reported adsorption phenomena on platinized platinum with other electrolytes, including HCl. They did not employ conductance methods, but titrated their abnormal solutions for total hydrogen and chloride ion concentration. According to them, in an hydrochloric acid solution, containing oxygen, the platinum black electrodes can adsorb an amount of hydrochloric acid which depends on the concentration. When the solution is

¹Frumkin and Donde, Ber., 60, 1816 (1927).

²Denham and Morris, Trans. Far. Soc., 24, 510 (1928).

³Kolthoff and Kameda, J. Am. Chem. Soc., 51, 2888 (1929).

replaced by another, and hydrogen is bubbled through, they believe that the hydrogen becomes adsorbed on the platinum black surface, forcing the previously adsorbed hydrochloric acid into the solution. This, of course, increases the acidity. If still another sample is introduced, and oxygen is bubbled, according to their theory the hydrogen is removed from the electrode surface, and hydrochloric acid is readsorbed. They observed a decrease of the acidity of this solution. The cycle of adsorption and desorption of hydrochloric acid could be repeated indefinitely, by the alternate bubbling of the two gases into fresh samples of the hydrochloric acid solution.

The results of the conductance data and of the titration data, which appear in columns four and five of Table VI, can be explained with the theory of Kolthoff and Kameda. During the preliminary rinsing of the cell, the equilibrium amount of hydrochloric acid was adsorbed on the platinized surface of the conductance cell electrodes. Therefore, no hydrochloric acid was either surrendered to the solution, or removed from it, when samples were introduced for the determination of the standard resistance. The hydrochloric acid was still adsorbed on the electrodes of the conductance cell, when hydrogen was bubbled into sample one. This forced the hydrochloric acid into the solution and the resistance decreased 2.36 per cent, and the amount of NaOH required to titrate the solution increased 2.13 per cent. Between samples one and two, the cell electrodes were rinsed with a fresh sample of the 0.01 M HCl solution for about one minute. The subsequent 2.47 per cent fall in resistance of sample two when hydrogen was bubbled through it in the cell indicates that considerable hydrochloric acid was adsorbed by the electrodes during their brief contact with the rinsing solution.

When the solution which followed a low resistance HCl-H₂ solution in the cell was saturated with oxygen (solutions 3 and 5), with nitrogen (solution 11) or allowed to stand in contact with the air (solution 14), hydrochloric acid was adsorbed from the solution on the platinum black electrodes, causing a decrease in the acidity of the solution and an increase in the observed resistance.

After the equilibrium amount of hydrochloric acid had been adsorbed, a new solution could be placed in the cell and oxygen (solutions 6 and 9a) or nitrogen (solutions 8 and 12) could be bubbled through the solution with very little change in the acidity or in the resistance. The electrodes already held all of the hydrochloric acid which they could adsorb. Likewise, when a low resistance hydrogen solution was removed and replaced with a fresh sample and hydrogen was bubbled again, there was but a slight change in the final resistance value, and the titration of the acidity showed that the solution was of nearly the same concentration as the standard solution. The electrode was previously covered with adsorbed hydrogen, and it remained in that condition. Therefore, no hydrochloric acid could become adsorbed on the electrodes (solution 10).

Solution 9b was titrated to determine whether or not the chloride ion, like the hydrogen ion, was changing in concentration. The titration indicated that it was (Table VI, 9b). Other chloride analyses were made in the next series of experiments (Table VII).

If this adsorption theory is correct, the adsorption of a given quantity of hydrochloric acid on the electrodes should not change the acidity and the resistance as much if a larger volume of solution is used. Solution 14 illustrated this. Twenty-five cubic centimeters more of the same 0.01 M HCl was added to the

usual 26.5 cc., in the glass cell. Solution 14 followed a low resistance hydrogen solution; hydrochloric acid was adsorbed from the solution on the electrodes, therefore, but the acidity and the conductivity decreased only 1.5 per cent instead of the 2.3 to 2.6 per cent change obtained in the previous solutions.

Only about half as much solution as usual was placed in the cell for solution 15. The resistance decreased 3.77 per cent when hydrogen was bubbled, much more than usual. This was assumed to be caused by the liberation of the hydrochloric acid adsorbed on the electrodes into a smaller volume of solution, producing a greater change in hydrochloric acid per unit volume.

The results reported above make it appear that oxygen and nitrogen gases are very similar in action, but in all cases, the electrodes were exposed to the air when the hydrogen solution was removed, before the new solution to be saturated with nitrogen was introduced into the cell. A different behavior was noted when nitrogen was bubbled into a certain low resistance 0.01 M HCl-H₂ solution. After one hour of bubbling the resistance had risen only 0.05 per cent above the low resistance attained when the bubbling of the hydrogen had been discontinued. After the bubbling had been continued for six and one quarter hours, the resistance of the solution had returned nearly to its standard value. This experiment indicated that the process by which hydrogen was removed from the platinum black electrodes, and replaced with adsorbed hydrochloric acid was much different in the experiments with oxygen and with nitrogen gases. If instead of nitrogen, oxygen was bubbled at the same rate into the low resistance HCl-H₂ solution, the resistance almost always rose rapidly after eight to fifteen minutes. Probably the oxygen combines with the hydrogen at the surface of the platinum black to form a small

amount of water, whereas the main action of the nitrogen is probably to carry off the hydrogen from the solution. The partial pressure of the hydrogen is thus reduced, and the amount left on the platinum black decreases accordingly.

To study the changes in chloride ion concentration, the 0.01 M HCl solution was used to produce a series of high and low resistance solutions, which were analyzed for chloride as follows: samples were removed from the conductance cell and weighed. The weighed portions were first titrated with 0.01 M NaOH and phenolphthalein as indicator. The pink color was then removed by the addition of three drops of 0.01 M nitric acid. Then 1.5 cc. of 0.1 M potassium chromate solution was added, and the titration with 0.01 M silver nitrate solution was carried on in an electrically lighted room with the shades drawn. Gradual darkening of the solutions was prevented in this way, and a fair end-point was obtained. It was more difficult, however, to obtain a sharp end-point in this chloride titration than in the acid-base titrations.

Later, the method of analysis was modified to facilitate the titration of both the total hydrogen ion and total chloride ion concentrations in one sample. The acid was titrated with 0.01 M NaOH. Three drops of a 0.03 per cent solution of methyl red, the indicator, was introduced from a burette to produce uniform drops. As in the previous acid-base titrations, the residue from the titration of the standard hydrochloric acid solution was preserved in a small beaker, so that the indicator colors might be matched.

After the determination of the end-point of the acid-base titration, a few more drops of NaOH were added until the solution had a clear yellow color. Then 1.5 cc. of 0.1 M potassium chromate solution was introduced, and the chloride analysis

performed as before. The results of these analyses appear in Table VII.

TABLE VII

CHLORIDE ANALYSES OF SOLUTIONS REMOVED FROM CONDUCTANCE CELL

Sample No.	Gas Bubbled	Per cent decrease In resistance	Per cent Increase in AgNO ₃ required	Per cent Increase in NaOH required
1	H ₂	1.5	1.3	
2	H ₂	2.3	2.5	
3	O ₂	-3.0	-2.5	
4	H ₂	1.4	1.6	
5	O ₂	-1.5	-1.1	
Second Series				
6	H ₂	1.4	1.3	0.8
7	O ₂	-1.5	-1.0	-1.9
8	H ₂	1.3	1.1	1.0
9	O ₂	-1.5	-1.8	-1.6

All of the changes in chloride concentration agreed within 0.4-0.5 per cent with the corresponding changes in resistance. These discrepancies may be significant, but the agreement was about all that could be expected. Only 25 cc. of solution was available for each titration, and the solutions were very dilute. In no case was the discrepancy between corresponding percentages equivalent to more than two drops of the titrating solution. Therefore, the chloride and hydrogen ion concentrations both change in about equivalent amounts; the change in resistance in the conductance cell consequently is due largely to variations in the concentration of hydrochloric acid in the solution.

Effect of Change in Source of Hydrogen

In the previous experiments hydrogen from the electrolytic generator had been used. To ascertain whether there might be

some difference in the observed behavior, electrolytic tank hydrogen was bubbled into 0.01 M HCl in cell A. The resistance rose for a few minutes, then fell to a value lower than standard. This behavior was the same as that observed previously with hydrogen from the generator. In subsequent work, the tank hydrogen was used, as it was more convenient.

Effect of Volume Changes in Conductance Cell

A study was made next of the effect on the per cent of abnormality of changes in the volume of 0.01 M HCl solution introduced into cell A. A sample of 0.01 M HCl was introduced from a burette into cell A, and hydrogen passed through it until a constant, low resistance solution was obtained. The succeeding sample was introduced into cell A with no intermediate rinsing, and the gas shown in Table VIII was bubbled through it. Each sample upon removal from cell A was analyzed in cell C. Cell A was inverted and drained for a half minute, and the large hanging drop was removed with filter paper.

TABLE VIII
EFFECT OF CHANGE IN VOLUME OF SOLUTION EMPLOYED
IN CONDUCTANCE CELL

Sample No.	Gas Used	Volume of Solution cc.	Per cent Decrease in Resistance	Per cent Increase In concentration C moles per liter	Moles HCl x 10 ⁶ gained by solution
1	O ₂	50	-1.46	-1.46	-7.30
2	H ₂	50	1.44	1.49	7.45
3	O ₂	50	-1.47	-1.47	-7.35
4	H ₂	50	1.35	1.39	6.95
5	O ₂	50	-1.47	-1.47	-7.35
6	H ₂	40	1.59	1.64	6.56
7	O ₂	40	-1.89	-1.88	-7.52
8	H ₂	30	2.32	2.42	7.26
9	O ₂	30	-2.16	-2.15	-6.45
10	H ₂	20	2.99	3.13	6.26
11	O ₂	20	-3.38	-3.31	-6.62

Unfortunately, it was not possible to use cell D (unplatinized electrodes) for these analyses because the cell constant was such that a good sound minimum could not be obtained with 0.01 M solutions. Cell C, with electrodes plated from a PtCl_4 solution which contained no lead acetate, was therefore used as the analyzing cell. Since hydrochloric acid solutions containing hydrogen were affected slightly by these electrodes, such solutions were removed from cell A, placed in four ounce bottles and oxygen bubbled through them for about one hour, before they were placed in cell C for analysis. Solutions containing oxygen were transferred directly from cell A to cell C.

The results of this investigation are given in column four of Table VIII, and indicate that the per cent deviation from the standard resistance increases as the volume of solution is reduced.

According to the Kolthoff-Kameda theory, if a certain amount of hydrochloric acid is adsorbed on the platinized surface from an hydrochloric acid solution containing oxygen, the same amount should be liberated when hydrogen is bubbled into the succeeding solution. To test this theory it was necessary to determine the actual amount of hydrochloric acid removed from or added to the various solutions. This required a knowledge of the concentration of each, which was determined from the corresponding resistance measurements and the equivalent conductance of the hydrochloric acid.

The following equation for the calculation of the equivalent conductance, Λ , of a solution of C moles per liter, has been determined by Mac Innes and Shedlovsky:¹

$$\Lambda = 426.04 - 156.70 \sqrt{C} + 165.0 C (1 - 0.2272 \sqrt{C}) \quad (1)$$

¹Mac Innes and Shedlovsky, J. Am. Chem. Soc., 54, 1429 (1932).

Values for Δ were calculated for a series of values of C. The specific conductance, k, of these solutions was then calculated by means of the usual formula

$$k = \frac{(\Delta)(C)}{1000}$$

Then the resistance, R, was calculated, by use of the relationship

$$R = \frac{K}{k}$$

where K was the cell constant of the conductance cell employed (cell C). A plot was made of CR vs. R. By the use of this plot, C values were calculated easily from the values of R which were determined experimentally in the conductance cell.

The per cent changes in C thus calculated are tabulated in column five of Table VIII. From these values and the actual volumes of solution in the cell, the number of moles of hydrochloric acid gained or lost by the various samples was computed, and tabulated in column six. It is to be observed that the quantity of acid lost by each oxygen containing solution is very nearly equal to the amount of acid given up to the succeeding sample when hydrogen was passed through. The agreement is especially significant between the members of each of the last three pairs, because of the changes in volume. Except in one pair, the gain in the hydrogen solution is a little less than the loss in the preceding oxygen solution. Later experiments indicated that these differences may be significant, but they corresponded to an error in the resistance measurement of 0.02 to 0.05 per cent.

Adsorption or Reaction with Walls of Storage Containers

In a new series of experiments, high or low resistance solutions were prepared in cell A, then removed and stored in dried, four ounce soft glass bottles, equipped with ground glass stoppers, until they could be analyzed in cell C. This procedure proved to

be unsatisfactory although the only difference in technique between this method and the one used in previous experiments was the use of dried soft glass bottles, instead of bottles wet with approximately the same strength hydrochloric acid solution. One solution, the resistance of which was 1.87 per cent lower than standard when measured in cell A, exhibited a resistance only 0.73 per cent lower than standard when measured in cell C, after storage in a dried soft glass bottle. The resistance of another solution was 0.10 per cent lower than standard in cell A, but after storage in a dried, soft glass bottle, its resistance in cell C was approximately 0.9 per cent higher than standard.

To investigate the role played by the walls of the bottles a portion of the 0.01 M HCl solution from the three liter quartz flask was allowed to stand in a dried, soft glass bottle for twenty-seven minutes, and then analyzed in cell C. The resistance had increased 1.09 per cent. In a second experiment, the standard 0.01 M HCl solution was allowed to stand in another dried, soft glass bottle for twenty-three hours. The resistance of this solution in cell C was about 0.7 per cent greater than standard. Evidently, hydrochloric acid had been adsorbed on the walls of the bottle, or had actually reacted with the glass, as claimed by Kraus and Parker.¹ The remainder of the solution from the first soft glass bottle was discarded, the bottle was rinsed with the standard 0.01 M HCl solution, and a second portion was left in the bottle for two and one-half hours. The resistance in cell C at the end of this time was within 0.02 per cent of the resistance of the standard hydrochloric acid solution. This indicated that initial adsorption or reaction had caused most of the trouble, and that further removal of hydrochloric acid from the 0.01 M

¹Kraus and Parker, J. Am. Chem. Soc., 44, 2429 (1922).

solution by reaction with the glass walls was negligible during a two and one-half hour period.

To ascertain the effect of a longer storage time, a soft glass bottle which had been filled with the standard 0.01 M HCl solution for two days, was rinsed twice with the standard 0.01 M HCl solution, then half filled with a fresh portion. After twenty-four hours the resistance of a sample of this solution in cell C was about 0.08 per cent greater than standard. The remainder of the solution was left in the bottle another twenty-six hours, after which time the resistance had risen 0.06 per cent more. This slow rise in resistance over a long period of time was probably due to a reaction of the hydrochloric acid with the glass.

In order to obviate further trouble, all later samples were stored in one or the other of two small quartz flasks. These were kept filled with the standard hydrochloric acid solution between experiments. The flasks were not dried, because it was suspected that there is an adsorption of hydrochloric acid on quartz. Anderson¹ showed that adsorption or some similar phenomenon had changed the concentration of dilute hydrochloric acid solutions. He found, however, that after the walls had been in contact several hours with a certain solution, the resistance remained essentially constant for not less than three weeks. His observations were confirmed in this work.

Dependence of Adsorption on Concentration

In certain previous experiments with a given volume of solution in the cell, it was observed that the per cent of abnormality was greater the more dilute the solution. A series of experiments with 0.01, 0.005 and 0.001 M HCl was performed in

¹Anderson, op. cit., p. 38.

an attempt to obtain sufficient data so that an equation for the adsorption isotherm of hydrochloric acid on platinized platinum could be deduced. Exactly 35.00 cc. samples of the stock solution of hydrochloric acid were introduced into cell A from a burette. An abnormal solution was produced by the bubbling of hydrogen or oxygen through the sample while it was in the cell. The solution was removed and stored in one of the small quartz flasks until it could be analyzed in cell C. While they were in the quartz flask, oxygen was bubbled through those samples which contained hydrogen. The molarity, C , of each sample was obtained from the resistance in cell C and the graph of CR vs. R .

The results of one series of experiments with 0.01 M, a second series with 0.005 M, and a third series with 0.01 M HCl are given in Table IX. The amount of hydrochloric acid gained or lost by each sample was calculated from the volume of the sample, and the difference between its molarity and that of the standard; these are tabulated in column five of Table IX.

When hydrogen was bubbled into the first sample of each series, the resistance dropped to a low value, due to the liberation of hydrochloric acid which had been adsorbed from previous samples on the platinized electrodes. When hydrogen was bubbled into the second sample of a series, the constant resistance finally reached was nearly equal to that of the standard. The resistance of the third sample through which oxygen was bubbled, was high due to readsorption of hydrochloric acid on the electrodes. The fourth sample, through which oxygen also was bubbled, exhibited nearly the standard resistance. The small differences from standard resistance of the second hydrogen or oxygen samples are probably not significant. When a sample was removed from cell A, approximately 0.24 cc. remained on the walls and electrodes to

TABLE IX

Sample No.	Gas Used	Resistance in cell C, ohms	C, moles per liter (calculated)	Moles HCl x 10 ⁶	
				Gained by Solution	Gained per Pair

(a)

1	H ₂	422.71	.0104024	6.26	
2	H ₂	429.83	.0102275	0.14	6.40
3	O ₂	437.90	.0100361	-6.56	
4	O ₂	429.92	.0102252	0.06	-6.50
5	H ₂	422.73	.0104020	6.24	
6	H ₂	429.88	.0102262	0.09	6.33
7	O ₂	436.97	.0100579	-5.80	
8	O ₂	430.03	.0102226	-0.04	-5.84
Std.	..	429.99	.0102236		

(b)

1	H ₂	831.92	.00523712	4.42	
2	H ₂	852.68	.00510816	-0.09	4.33
3	O ₂	877.25	.00496349	-5.16	
4	O ₂	851.28	.00511665	0.20	-4.96
5	H ₂	831.10	.00524234	4.60	
6	H ₂	852.12	.00511159	0.03	4.63
7	O ₂	875.11	.00497578	-4.73	
8	O ₂	853.07	.00510579	-0.18	-4.91
Std.	..	852.24	.00511086		

(c)

1	H ₂	424.54	.0103569	4.62	
2	H ₂	429.72	.0102302	0.18	4.80
3	O ₂	437.38	.0100482	-6.19	
4	O ₂	429.98	.0102238	-0.04	-6.23
5	H ₂	422.88	.0103982	6.06	
6	H ₂	429.69	.0102308	0.20	6.26
7	O ₂	437.44	.0100470	-6.23	
8	O ₂	430.07	.0102217	-0.12	-6.35
9	H ₂	423.24	.0103893	5.75	
10	H ₂	429.88	.0102262	0.04	5.79
Std.	..	429.93	.0102250		

admix with the subsequent sample. This error alone accounts on the average for nearly half of the observed differences from the standard resistance of the second hydrogen or oxygen samples, although it represents an error of only 0.01 per cent in the

resistance of the solution. Other errors might be caused by slow attainment of equilibrium between the hydrochloric acid on electrodes and in the solution, or by the slow diffusion of hydrochloric acid from the inside of the platinized surface of the electrodes.

There was an error also in the first hydrogen or oxygen sample of each pair due to a small amount of solution which adhered to the cell walls and to the electrodes. This error was in the opposite direction to the corresponding error in the second hydrogen or oxygen sample, and nearly compensated for it. Consequently, the samples were grouped in pairs; two successive samples through which hydrogen was bubbled constituted one type of pairs, and two successive samples through which oxygen was bubbled constituted the other type of pairs. The gain of hydrochloric acid per pair was calculated from the results of column five, Table IX, and appears in column six.

If it is assumed that the Freundlich adsorption isotherm applies to the adsorption of hydrochloric acid on platinized platinum, the value of the constants can be evaluated from the data of Table IX. By the method of least squares, the following equation was found to represent the behavior of that electrode:

$$\log x = -4.50 + 0.361 \log c \quad (2)$$

where x represents the number of moles of hydrochloric acid adsorbed on the electrodes of cell A, in the presence of a hydrochloric acid solution of concentration c moles per liter.

In an attempt to obtain more information concerning the adsorption isotherm, a series of measurements was made with an approximately 0.001 M HCl solution. Since a good sound minimum could be obtained in cell D (unplatinized electrodes) with 0.001 M solutions, it was employed for the analysis of samples removed

from cell A. It was not necessary to remove hydrogen from the samples containing it, before analysis since the presence of hydrogen produced no abnormal effects in cell D. The standard value for the approximately 0.001 M HCl was determined in cell D at the beginning of the series, and again at the end of a week. The second value was only 0.01 per cent less than the original. This illustrated the stability of dilute hydrochloric acid solutions when stored in the three liter quartz flask.

The results of the series with 0.001 M HCl are given in Table X. The amounts apparently adsorbed on the electrodes from the samples through which oxygen was bubbled in cell A, were one and a half to two times as great as the amount desorbed from the electrodes in the samples through which hydrogen was bubbled (column 6). This same type of discrepancy was smaller but apparent in the 0.005 M series and was barely detectable in the second 0.01 M series (Table IX, column 6). Some secondary effect was becoming of increasing importance, as more dilute solutions were studied, and was so large in the 0.001 M solutions that the data were of little value in the determination of the adsorption isotherm. It may be significant that two values for the amount adsorbed on the electrodes in an oxygen atmosphere were in approximate agreement with equation 2. An extrapolation of that equation to 0.001 M indicated that the amount adsorbed should have been 2.63×10^6 moles, compared with the observed oxygen values of 2.53 and 3.42×10^{-6} moles.

Time Variations in Resistance of Samples Through Which Hydrogen or Oxygen was Bubbled

While only the final resistance has been given in Table X, measurements were made every five or ten minutes, and sometimes every minute or two, to follow the changes of resistance. The

TABLE X

RESISTANCE MEASUREMENTS WITH 0.001 M HCL

Sample No.	Gas Used	Resistance, ohms		C, moles per liter $\times 10^3$	Moles HCl $\times 10^6$ Gained by Solution	% decrease In Resistance	
		Cell A	Cell D			Cell A	Cell D
Std.		366.45	5683.7	1.0213 ₄			
3	H ₂	349.79	5427.9	1.0697 ₅	1.69	4.55	4.50
4	H ₂	366.22	5678.1	1.0223 ₄	0.04	0.06	9.10
5	O ₂	402.18	6230.5	0.9312 ₃	-3.15	-9.75	-9.62
6	O ₂	369.15	5726.5	1.0137 ₆	-0.26	-0.74	-0.75
7	H ₂	351.06	5442.5	1.0668 ₆	1.59	4.20	4.24
8	H ₂	366.18	5681.0	1.0218 ₂	0.02	0.07	9.05
9	O ₂	391.08	6061.5	0.9573 ₃	-2.24	-6.72	-6.65
10	O ₂	369.60	5729.5	1.0131 ₂	-0.29	-0.86	-0.81
11	H ₂	351.21	5450.2	1.0653 ₄	1.54	4.16	4.11
12	H ₂	366.78	5679.0			-0.09	0.08
13	O ₂	391.06	6054.6			-6.72	-6.53
14	O ₂	368.04	5708.5			-0.43	-0.44
15	H ₂						
	(peak)	390.00	6032.0			-6.43	-6.12
16	H ₂	340.54	5288.0			7.07	6.97
17	O ₂	approx.				approx.	
	(peak)	440.00	6469.0			-20.10	-13.81
18	H ₂	328.28				10.42	
18	H ₂	330.64					
18	H ₂	334.93					
18	H ₂	337.22					

variation of the resistance of solutions 7 and 11 in cell A is shown in Figure 5. These curves are typical of the general trend of the resistance of all samples through which hydrogen was bubbled. In each case the preceding solution had contained dissolved oxygen. The electrodes were therefore in their "normal" condition; that is, they held an amount of absorbed hydrochloric acid which can exist in equilibrium with the standard solution. Consequently, the resistances at the start were nearly normal - 366.5 ohms. As hydrogen was bubbled, the resistances rose to peak values of approximately 397 ohms, then dropped rapidly to constant values of about 351 ohms.

The effect on the resistance in cell A of the bubbling of

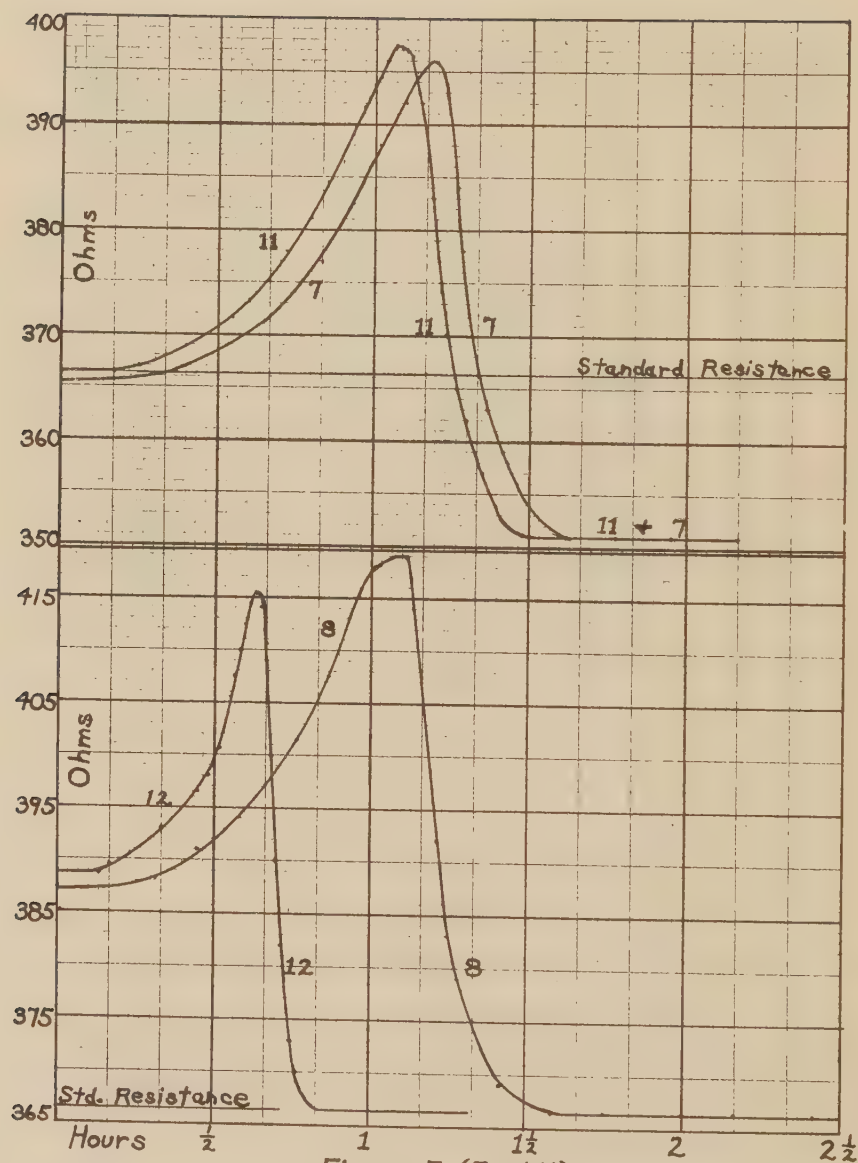


Figure 5 (7 and 11)

Figure 6 (8 and 12)

hydrogen into a sample of 0.001 M HCl when the solution previously in the cell also had been saturated with hydrogen, is shown in Figure 6. These curves are for solutions 8 and 12, of the 0.001 M series. The general shape of the curves is the same as those in Figure 5, but the resistances have shifted to higher values. The initial resistances were abnormally high (387-389 ohms) due to adsorption, occurring before the first measurement, of hydrochloric acid from the solutions onto the electrodes which had been previously covered with hydrogen. As hydrogen was bubbled, the resistances rose to hydrogen peaks of 415.5 and 419 ohms, then dropped rapidly to constant values which were within less than 0.1 per cent of the standard resistance.

A special series of experiments was performed with sample No. 15. This sample was left in cell A nearly three days, during which time hydrogen and oxygen were bubbled alternately into the solution. The results of the first day are shown in Figure 7. The resistance of this solution was standard (366.5 ohms) at the start, because oxygen had been bubbled through the two solutions previously in the cell. As hydrogen was bubbled, the resistance rose to a peak, a, then fell to a constant low value, b. This is a characteristic behavior (Figures 4 and 6). A few minutes after the bubbling of oxygen was started, the resistance rose rapidly toward an oxygen peak, c, reached the peak and fell slowly. The hydrogen peak, d, and low value, e, were nearly duplications of points a and b. The final low value, e, was only 1.5 ohms higher than the first low value, b.

When oxygen was again bubbled, the oxygen peak, f, was reached quickly. The oxygen supply was stopped two minutes later, and bubbling with hydrogen was begun. The hydrogen peak, g, was reached within a few minutes. The low hydrogen value, h, which

followed, was about half an ohm higher than the preceding low value, e.

When oxygen was bubbled next, an attempt was made to stop the oxygen supply before the oxygen peak was reached. Nevertheless, there was enough oxygen in the system to reach the peak, i. This peak and the following hydrogen peak, j, are quite similar to the corresponding peaks, f and g. The next time oxygen was bubbled, it was stopped after six minutes, and hydrogen was started at once. The resistance rose only a few ohms from the low value, k, to a low hydrogen peak, l, then fell to a new low value, m.

The next day (not shown in Figure) oxygen was bubbled until a resistance of 411 ohms had been reached. When the resistance had dropped to 386 ohms, oxygen was stopped and hydrogen started. After about thirty minutes a peak of 399 ohms was reached. Three or four minutes later the flow of gas was stopped, when the resistance had reached 397 ohms. The resistance continued to fall for about one and a half hours when it had become nearly the same as the previous low resistance, m. This showed that after the hydrogen peak had been reached, further bubbling with hydrogen was not necessary to cause the resistance to fall to a low value.

Oxygen was then bubbled through the solution until the oxygen peak had been passed and continued for an additional two hours. Then hydrogen was bubbled into the solution for thirty minutes. The flow was stopped before a hydrogen peak could be reached. Resistance measurements were continued for one hour and fifty minutes, but the resistance did not fall. It fluctuated between 392 and 395.5 ohms, i.e., it remained nearly 8 per cent higher than the normal resistance of 366.5 ohms. After an



Figure 7

intermediate bubbling with oxygen, this experiment was repeated; the bubbling of the hydrogen was stopped before the hydrogen peak was reached. Again, the resistance did not fall. It remained between 390 and 391 ohms for two and a half hours. Another experiment with solution 15 is described in the next section.

A Study of Hydrogen and Oxygen Peaks

Throughout the series of measurements with 0.001 M HCl (Table X) the peak resistances obtained when hydrogen was bubbled through a solution, through which oxygen had been bubbled previously, were remarkably concordant. These values for several samples are given in Table XI, to three significant figures. A greater precision would have been very difficult to obtain in solutions whose resistances were varying so rapidly.

TABLE XI

Sample No.	Hydrogen Peak Value, ohms
7	396
11	398
15	395
15	398
15	398
15	401
15	398
15	399

The observations that a hydrogen peak always precedes a low resistance hydrogen solution, that the peak value is nearly a constant resistance, and that hydrogen must be bubbled until the peak is passed, if the low resistance value is to be attained indicate that some change is occurring in the solution, most likely at the surface of the platinized electrodes, which must precede the forcing of hydrochloric acid from the electrode surface into the solution. Before hydrogen was bubbled through

any of the samples mentioned in Table XI, the resistance was practically standard (because the previous samples contained oxygen). The electrodes held (adsorbed) the normal amount of hydrochloric acid. When hydrogen was bubbled, the resistance rose first to a hydrogen peak, before it fell to a value lower than standard. The reason for this peculiar resistance effect was a mystery. The data indicated that a quantity of hydrochloric acid in addition to the normal amount had become adsorbed on the electrodes, and that when the bubbling of hydrogen was continued, this additional quantity together with the normal amount was desorbed from the electrodes. To test this assumption, hydrogen was bubbled into solution 15, after a bubbling with oxygen. The bubbling with hydrogen was continued until the hydrogen peak was reached, at which time the resistance in cell A was 6.43 per cent. greater than the standard. The solution was then removed from the cell as rapidly as possible, and analyzed in cell D. Its resistance in this cell was 6.12 per cent greater than that of the standard solution. This proved that the conductance of the solution as a whole had decreased greatly.

The resistance of the succeeding sample (No. 16) in cell A fell finally to a constant value of 340.54 ohms, when hydrogen was bubbled through the solution. The resistance of this sample when analyzed in cell D was 6.97 per cent lower than standard. The resistances of samples 3, 7 and 11 (Table X) fell to 349.8-351.2 ohms, when hydrogen was bubbled, and the resistances of these solutions were 4.11-4.50 per cent lower than standard, when analyzed in cell D. It was assumed that the electrodes held, adsorbed, approximately the normal amount of hydrochloric acid before each of the three samples were introduced, because oxygen had been bubbled through the samples which preceded them in the

cell. A drop in resistance to approximately 350 ohms (about 4.3 per cent lower than standard) was due, therefore, to the liberation from the electrodes of the normal amount of hydrochloric acid. It was concluded from the results obtained with sample No. 16 that more than the normal amount of hydrochloric acid had become adsorbed on the electrodes from sample No. 15.

To ascertain whether an oxygen peak also represented an adsorption on the electrodes of hydrochloric acid in excess of the normal amount, hydrogen was bubbled into the next sample, No. 17. After a preliminary hydrogen peak, the final constant resistance was 366.85 ohms, very nearly the standard value of 366.5 ohms. This was to be expected, since the electrodes were in contact with dissolved hydrogen in the previous sample. When oxygen was bubbled into this solution, the resistance rose rapidly to a peak of about 440 ohms. The solution was removed from cell A as rapidly as possible. Its resistance was 13.81 per cent higher than standard, according to a subsequent measurement in cell D. This proved that the oxygen peak, too, corresponded to a change taking place throughout the solution. Evidently, here also conditions were favorable for a temporary adsorption of an amount of hydrochloric acid in excess of the normal quantity. To prove this, hydrogen was bubbled into the next sample, No. 18. After a preliminary hydrogen peak, the resistance fell to 328.28 ohms, 10.42 per cent lower than standard, whereas the usual drop was 4.1-4.2 per cent.

To make certain that most of the changes in resistance accompanying a hydrogen or an oxygen peak were due to actual loss of hydrochloric acid from the solution to the electrodes, samples were removed from cell A near a hydrogen or oxygen peak, and titrated. Nessler tubes were employed in the titration of these

approximately 0.001 M hydrochloric acid solutions. Twenty-six and a half cubic centimeters of the sample was transferred to a 50 cc. Nessler tube, three drops of 0.03 per cent solution of methyl red added from a burette, and the titration carried out with approximately 0.001 M NaOH solution, to a color arbitrarily selected as the end-point in a similar titration of the standard solution. To produce a uniform mixing of the contents of the Nessler tube, especially near the end-point, it was closed with a rubber stopper and turned end for end several times. The end-point could be obtained with a precision of about one drop of the titrating solution. The results obtained in a series of experiments are given in Table XII.

TABLE XII

Sample No.	Gas Used	Per cent decrease In resistance, cell A	Per cent increase In NaOH
6	H ₂	4.33	3.98
7	none	-8.45	-8.44
8	H ₂ (peak)	-4.92	-4.95
9	H ₂	10.62	10.85
10	O ₂ (peak)	-13.40 (approx.)	-12.80
11	H ₂	10.33	10.36
12	none		-8.11
13	H ₂	6.02	5.49

The data of Table XII indicated that almost all of the changes in resistance over a hydrogen or an oxygen peak were due to a disappearance of hydrochloric acid from the solution. Thus sample 8 (Table XII) was removed from the cell (A) near the hydrogen peak, when the resistance was 4.92 per cent greater than normal. In the succeeding titration, 4.95 per cent less NaOH was used than was required to titrate the same volume of standard solution. Sample No. 10 was removed from the cell near an oxygen

peak. The titration required 12.8 per cent less NaOH than for the standard solution, whereas the resistance was approximately 13.4 per cent greater than standard. This was a satisfactory agreement as it was impossible to make an accurate resistance measurement near an oxygen peak. The change in resistance was so rapid that it might vary several per cent between the time it was measured and the time of removal of the solution from the cell.

Sample No. 12 was placed in the cell following the removal of a low resistance solution, containing hydrogen (No. 11). Sample No. 12 was left in the cell one and one half minutes. No oxygen was bubbled. A subsequent titration with 0.001 M NaOH showed that 8.11 per cent of the hydrochloric acid originally present had disappeared; i.e., this hydrochloric acid had been adsorbed rapidly on the electrodes, even though no oxygen had been bubbled.

Range of Minimum Sound in Measurement of Resistance

For most of the resistance measurements, the range of minimum sound in the telephones was small, corresponding to about 0.5 of a scale division on the slide wire of the Wheatstone bridge (corresponding to .02 per cent error in the resistance). Within this range there was almost complete silence in the phones. However, as the resistance neared a hydrogen peak, the minimum extended over a wider range on the slide wire, and there was sound in the phones throughout the range. As soon as the resistance peak was passed, the minimum range narrowed, and it was always excellent at the low resistance value. Near an oxygen peak, the minimum range often extended over two to four scale divisions, but as soon as the peak was passed, the minimum range began to narrow rapidly. The reason for this behavior is not

known.

Effect of Gas Bubbles on the Resistance

It was noticed many times that the resistance measurements over a hydrogen peak were not the same just before a gas bubble passed between the electrodes and just after a bubble passed. On the part of the curve corresponding to an increase in resistance the resistance fell 3-5 scale divisions on the slide wire (0.12-0.20 per cent) immediately after a hydrogen bubble passed, but rose even more before the next bubble. That is, the general trend in resistance was toward higher values, but the resistance fell after each bubble of gas. After the hydrogen peak was passed, the conditions were reversed. The resistance rose 1-3 scale divisions on the slide wire (0.04-0.12 per cent) after each bubble of hydrogen, but fell even more before the next bubble of hydrogen. The bubbles were four to six seconds apart. The difference between the two values was greater when the rate of bubbling was slower. As the constant low resistance was approached the difference between the values just before and just after the bubbles became less, and disappeared when the constant value was reached.

The effect on the resistance of the passage of a gas bubble through the solution may be explained as follows: at first, hydrochloric acid was being adsorbed on the electrodes. This adsorption removed some hydrochloric acid from the solution between the electrodes, and caused the resistance to rise. When a bubble of hydrogen passed, the solution was stirred, and became of more uniform composition throughout the cell, and an instantaneous decrease in resistance resulted. However, since hydrochloric acid was being adsorbed on the electrodes continuously, the general trend in the resistance was toward higher values.

After the peak had been passed, the conditions were reversed. Hydrochloric acid was coming from the electrodes into the solution. Hydrochloric acid concentration between the electrodes increased, and the resistance decreased. When a hydrogen bubble passed, the solution between the electrodes was swept into the main body of the solution, and the resistance rose temporarily. However, since the electrode was losing hydrochloric acid to the solution continuously, the general trend in the resistance was downward.

Oxidation of Chloride Ion in the Conductance Cell

When hydrogen and oxygen were bubbled alternately through a given sample (Figures 4 and 7), a progressive rise occurred in the hydrogen minimum resistance (b, e, h, k, m, Figure 7). It seemed likely that some hydrochloric acid was being removed from the solution. Since the partial pressure of hydrochloric acid in such dilute solutions is far too low for any appreciable amount to be carried off as gas, it seemed likely that hydrochloric acid was being oxidized to Cl_2 or one of its higher oxidation products.

Further evidence of the permanent removal of hydrochloric acid from solutions was found in the data of Tables IX and X. Usually more hydrochloric acid disappeared from a high resistance sample (as No. 5, Table X), through which hydrogen was bubbled, than was recovered in a succeeding low resistance sample (as No. 7, Table X), through which hydrogen was bubbled.

To ascertain whether Cl_2 or one of its higher oxidation products was formed in small amounts in the conductance cell, oxygen was bubbled through a low resistance HCl-H_2 solution (originally 0.001 M) in cell A until the oxygen peak had been passed. No yellow color was produced when titanium sulfate was added to a portion of this solution, which indicated that H_2O_2

was absent. Another portion of the sample, however, liberated a small amount of iodine from potassium iodide in acid solution, and this behavior demonstrated the presence in the sample of some oxidizing agent.

The formation of some substance other than H_2O_2 in the $HCl-H_2$ samples in cell A was indicated by the peculiar action of some of these samples on a suspension of cupric hydroxide. The use of cupric hydroxide was recommended by Quartaroli¹ as a sensitive test for H_2O_2 . The procedure employed was as follows: five cubic centimeters of a 3 per cent cupric sulfate solution was added to 20 cc. of the sample from the conductance cell, the solution made alkaline with 2 cc. of 18 per cent NaOH solution, and heated to 50°C. in a water bath. A control tube, containing 20 cc. of the standard hydrochloric acid solution from the three liter quartz flask was treated in the same manner. The color of the cupric hydroxide precipitate changed more or less rapidly in each tube from bright blue to green, then gray-green, and finally black, but the presence of a very small amount of H_2O_2 accelerated this conversion. One part H_2O_2 in 6,000,000 parts of water could be detected easily in specially prepared solutions of known strength, by the increased rate of conversion of the blue precipitate to green color. The cupric hydroxide test for H_2O_2 was used in conjunction with the titanium sulfate and tartaric acid methods (p. 33) to detect traces of H_2O_2 in $HCl-H_2$ samples removed from cell A. Positive tests for H_2O_2 were obtained twice, but on three other occasions the solution removed from the cell decelerated the color change of the cupric hydroxide; i.e., the precipitate in the solution from the cell remained a blue color for several minutes after the precipitate in the control sample had

¹Quartaroli, Gass. chim. ital., 55, 264 (1925); C. A., 19, 3054 (1925).

turned a definite green color. At that time the formation of some oxidation product of chloride ion in HCl-H₂ solutions was not suspected. Other substances such as chlorplatinic acid, lead acetate, oxygen and hydrogen were dissolved in a dilute hydrochloric acid solution, and the cupric hydroxide test applied. Such solutions changed the color of the cupric hydroxide at the same rate or a little more rapidly than the control. However, when the test was applied to a very dilute chlorine solution, a marked decelerating effect was noted. These results were in accord with the indication of the iodine reaction that chlorine or one of its oxidation products was present in HCl-H₂ samples.

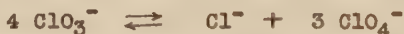
According to the International Critical Tables,¹
 $K = 4.7 \times 10^{-4}$ for the following equilibrium:



Therefore, in a 0.001 M HCl, the ratio of hypochlorous acid to chlorine is about 470. Hypochlorous acid decomposes very slowly, according to the equilibrium



Chlorate ion, in turn, decomposes very slowly, as follows:



The actual concentration of Cl₂, HClO, ClO₃⁻ and ClO₄⁻ in a certain hydrochloric acid solution depends on the concentration of hydrochloric acid, the numerical value of the various equilibrium constants, and the speeds with which the equilibria are attained. It is believed that under the conditions which existed in the conductance cell, HClO was the principal oxidation product.

A new series of measurements was made, with a 0.001180₉ molar hydrochloric acid solution to ascertain if the amount of hydrochloric acid oxidized could account approximately for the

¹International Critical Tables, McGraw-Hill Book Co., Inc., New York, 1930, Vol. VII, p.234.

discrepancy between the amount of hydrochloric acid which disappeared from a high resistance solution and the amount of hydrochloric acid recovered from the subsequent low resistance solution, through which hydrogen was bubbled. The technique was similar to that employed in the previous 0.001 M series (Table X) except that no oxygen was bubbled into the two or three samples in cell A which succeeded the low resistance sample through which hydrogen was bubbled. Bubbling of oxygen was found to be unnecessary, since readsorption of hydrochloric acid on the electrodes occurred without it; any error due to loss of chlorine or hypochlorous acid from the solution by a prolonged bubbling with oxygen was thus avoided, as well as the error produced by the oxidation of KI by oxygen. The results of these experiments are given in Table XIII. This table contains a record of three series of measurements - samples 1-4, 5-7, and 8-10. Each series was terminated when the resistance of a new sample was not changed appreciably when the electrodes were immersed in it. This last sample of each series was not recorded in Table XIII. Since no resistance changes occurred in this last sample, it was not analyzed for HClO and the irrelevant resistance data were not recorded in Table XIII. As a matter of fact, the last sample of each of the first and second series was used as the initial sample of the subsequent series.

To determine the amount of hydrochloric acid oxidized, 26.5 cc. of the 40.00 cc. sample removed from cell A after the final resistance measurement was introduced into a 50 cc. Nessler tube; 2 cc. of 5 per cent KI and 3-4 drops of concentrated hydrochloric acid were added. In a control tube, 26.5 cc. of the standard hydrochloric acid solution was substituted for the solution from the cell. The tubes were closed with a rubber

TABLE XIII

Sample No.	Gas Used	R ohms	Na ₂ S ₂ O ₃ cc.	Moles HCl, in 40 cc. solution, x 10 ⁶				
				Gained by Soln.	Lost from Soln.	Lost by Oxid.	Desorbed from Elec-trodes	Adsorbed on Elec-trodes
Std.	..	316.96						
1	H ₂	311.50	0.96	0.83		0.39	1.12	
2	..	329.49	1.13		1.81	0.46		1.35
3	..	316.05	0.39	0.14		0.16	0.30	
4	..	317.19	none		0.04			0.04
5	H ₂	307.00	0.91	1.54		0.37	1.91	
6	..	330.25	0.47		1.91	0.19		1.72
7	..	316.85	none	0.02			0.02	
8	H ₂	305.42	0.54	1.79		0.22	2.01	
9	..	330.59	none		1.96			1.96
10	..	315.77	none	0.18			0.18	

stopper and inverted several times during an hour.¹ Then 2 cc. of 1 per cent starch solution was added, and the solution was titrated with 0.00082 N Na₂S₂O₃. Near the end-point, the tube was stoppered and inverted several times after the addition of each drop of the titrating solution. The end-point could be estimated within one drop of the titrating solution. Usually no blue color developed in the control tube. The Na₂S₂O₃ solution was standardized with recrystallized KBrO₃. A 0.1 N KBrO₃ solution was diluted to form a 0.001 N solution, and samples of the diluted solution were titrated with the Na₂S₂O₃ solution in the same manner described above.

The molarity of HCl, C, of each sample removed from cell A was calculated from the observed resistance, R, Table XIII, column 3, and a plot of CR vs. R. The product of (0.04000) (C) gave the number of moles of hydrochloric acid in the 40.00 cc. of solution in the cell. The difference between this value and the number of moles of hydrochloric acid in 40.00 cc. of the

¹Makower and Bray, J. Am. Chem. Soc., 55, 4765 (1933).

standard solution is recorded in columns 5 and 6 of Table XIII.

The moles of $\text{Na}_2\text{S}_2\text{O}_3$ consumed was equal to the number of equivalents of HClO (or other oxyacid of chlorine) reduced. The reduction of chlorate by iodide is so slow that it is not probable that any appreciable fraction of the chlorate was reduced during the hour. The number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ used was therefore assumed to be twice the number of moles of HClO present, and if no appreciable amount of chlorate was formed, was equal to twice the number of moles of HCl oxidized. The amount of hydrochloric acid oxidized, calculated in accordance with these considerations is tabulated in Table XIII, column 7.

The moles of hydrochloric acid desorbed from the electrodes in any low resistance solution (column 8, Table XIII) was calculated as the sum of the moles of hydrochloric acid gained by the solution (column 5) and the moles of hydrochloric acid lost by oxidation (column 7). The moles of hydrochloric acid adsorbed on the electrodes in any high resistance solution (column 9) was calculated as the difference between the moles of hydrochloric acid lost by the solution (column 6) and the moles of hydrochloric acid lost by oxidation (column 7). The moles of hydrochloric acid on the electrodes was nearly the same at the beginning and end of each series. Therefore, the amount desorbed from the electrodes should equal the total amount adsorbed. A summation into series, of the results of columns 5, 6, 8 and 9 of Table XIII is presented in Table XIV. The agreement between columns 4 and 5 of Table XIV is satisfactory. Better agreement could not be expected since each series involved the summation of the errors of seven to eleven operations; the errors included the introduction of exactly 40.00 cc. into the cell, the measurement of the resistance and the titration of the very small

amount of hydrochloric acid oxidized. An error of one drop in the $\text{Na}_2\text{S}_2\text{O}_3$ titration would change the results about 1 per cent. Nevertheless, on the whole, the correction applied was too large, and it is possible that the discrepancy is significant. The oxidation of Cl^- to ClO_3^- would not change the resistance greatly because chloric acid is a strong acid. If, however, a little ClO_3^- is reduced by iodide ion, the correction for oxidation would be too large. The presence of a small amount of H_2O_2 would also exaggerate this correction.

TABLE XIV

Series	Moles $\text{HCl} \times 10^6$			
	Gained by Samples	Lost by Samples	Desorbed from Electrodes	Adsorbed on Electrodes
1	0.97	1.85	1.42	1.39
2	1.56	1.91	1.93	1.72
3	1.97	1.96	2.19	1.96
Total	4.50	5.72	5.54	5.07
Average	1.40	1.91	1.85	1.69

The final series of measurements, recorded as separate samples in Table XV, and summarized into series in Table XVI, were performed to determine the relation between HClO production and the hydrogen and oxygen (or air) peaks (Figures 4, 5, 6, and 7). The technique was the same as in the previous series. The hydrochloric acid solution employed was 0.0009997_6 N .

The measurement of the resistance of sample no. 10, in series 3, was very unreliable because the resistance was changing so rapidly over the oxygen peak that an accurate reading was impossible. If this series (3) is omitted, an excellent agreement is obtained between the moles of hydrochloric acid adsorbed on

TABLE XV

Sample No.	Gas Used	R ohms	Na ₂ S ₂ O ₃ cc.	Moles HCl, in 40 cc. sample, $\times 10^6$				
				Gained by Soln.	Lost from Soln.	Lost by Oxidn.	Desorbed from Elec-trodes	Adsorbed on Elec-trodes
Std.	..	374.02						
4	H ₂	361.64	0.72	1.38		0.29	1.67	
5	..	392.72	none		1.91			1.91
6	..	370.97	none	0.33			0.33	
7	H ₂	399.52	0.63		2.57	0.26		2.31
8	..	356.53	none	1.97			1.97	
9	..	373.31	none	0.08			0.08	
10	H ₂ -O	387.?	0.93		1.37	0.38		0.99
11		357.81	none	1.82			1.82	
12		371.21	none	0.31			0.31	
13	H ₂	360.57	0.27	1.50		0.11	1.61	
14	..	401.24	none		2.73			2.73
15	..	365.00	none	0.99			0.99	
16	..	373.93	none	0.01			0.01	
17	H ₂	398.41	0.98		2.46	0.40		2.06
18	..	353.86	none	2.29			2.29	
19	..	372.12	none	0.21			0.21	

TABLE XVI

Series	Moles HCl $\times 10^6$			
	Gained by Samples	Lost by Samples	Desorbed from Electrodes	Adsorbed on Electrodes
1	1.71	1.91	2.00	1.91
2	2.05	2.57	2.05	2.31
3	(2.13)	(1.37)	(2.13)	(0.99)
4	2.50	2.73	2.61	2.73
5	2.50	2.46	2.50	2.06
Total, omitting series 3	8.76	9.67	9.16	9.01
Average	2.19	2.42	2.29	2.25

and desorbed from the electrodes (columns 4 and 5, Table XVI). If the removal of chloride ion by oxidation were neglected the calculated adsorption and desorption would have differed considerably (columns 2 and 3).

A small amount of HClO was present in the samples removed from the cell near a hydrogen peak (Nos. 7 and 17, Table XV) but only 15 per cent or less of the hydrochloric acid lost from the sample was due to the formation of HClO . Therefore, as indicated by previous experiments (Table XII) the adsorption of hydrochloric acid on the electrodes in excess of the normal amount explains the larger part of the increase in resistance over a hydrogen peak.

THEORY OF HYDROGEN-OXYGEN CYCLE

Several theories have been proposed to explain the catalytic properties of platinum black, which may account for the fact that an amount of hydrochloric acid in excess of the normal amount is sometimes adsorbed on the electrodes. The excess adsorption was illustrated by the peaks (a, c, d, f, g, i, j) of Figure 7, and is evident in the data of Table XII.

An intermediate compound theory was proposed by De la Rive¹ and others² to explain the catalytic properties of platinum black in hydrogenation reactions. An alternate oxidation of the platinum to PtO or PtO₂ and its reduction to the metal again, was postulated.

Richard Willstätter and Daniel Jaquet³ found that if a platinum electrode was initially loaded with oxygen, many reductions of organic compounds could be brought about with subsequent bubbling of hydrogen. As the catalyst gradually lost its oxygen, due to formation of water with the hydrogen, it could be reactivated by treatment with oxygen again. Ernst Waldschmidt-Leitz and Franz Seitz⁴ claimed also that the oxygen content of the platinum black determined the results obtained when hydrogenation was catalyzed by platinum.

¹De la Rive, Pogg. Ann., 46, 489 (1839).

²Brodie, Phil. Trans., 151, 855 (1862); Engler and Wöhler, Z. anorg. Chem., 29, 1 (1901); Wöhler, Ber., 584, 3475 (1903).

³Willstatter and Jacquet, Ber., 51, 767 (1918).

⁴Waldschmidt-Leitz and Seitz, Ber., 58 B, 563 (1925).

A de Gregorio Rocasolano¹ reported that during the preparation of a platinum electro-sol, only hydrogen was evolved. Later when the coagulum from the sol was heated, oxygen was given off. He opined that the particles were composed of platinum and an oxide of platinum.

The electrode potential variations when the gas around the electrode was changed rapidly from a hydrogen to an oxygen atmosphere and back, were studied by F. P. Bowden.² When the potential was changed from an oxygen to a hydrogen potential, a pause was obtained at 0.37 volt (against a saturated calomel electrode). This pause was longer, the longer the electrode had been in the oxygen atmosphere previously. Bowden believed that this pause was due to PtO_2 , and that it represented the equilibrium potential of this oxide in a solution saturated with hydrogen. Indeed, he produced a coating of PtO_2 on platinum by the burning of Pt wire in oxygen. The voltage of this PtO_2 covered wire remained at 0.37 volt for a long period in a solution saturated with hydrogen.

The following tentative theory was devised with the aid of the facts and the theories mentioned above, to explain the hydrogen and oxygen peaks, such as those shown in Figure 7: The surface of a "normal" electrode (obtained after several samples were placed in the cell and no gas was bubbled) was a layer of platinum oxide on which was adsorbed a definite amount of hydrochloric acid in equilibrium with a solution of a certain concentration. When hydrogen was bubbled through a solution, in equilibrium with the acid covered electrode, the resistance rose

¹de Gregorio Rocasolano, Nachr. Ges. Wiss. Gottingen, pp. 177-188 (1924); C. A., 20, 1348 (1926).

²Bowden, Proc. Roy. Soc. (London), A 125, 446 (1929).

from the normal value to a hydrogen peak, because during this time the platinum oxide was being reduced by the hydrogen presumably to platinum (or a lower oxide of platinum) on which hydrochloric acid was adsorbed in greater quantity. At the hydrogen peak all of the platinum oxide had been reduced to platinum, and this pure platinum surface adsorbed the maximum amount of hydrochloric acid from the solution. When the platinum oxide had been reduced, additional hydrogen arriving at the surface was adsorbed, displacing the adsorbed hydrochloric acid. A constant, low resistance was obtained when all of the removable hydrochloric acid had been forced into the solution by the adsorbed hydrogen. K. A. Hofmann¹ assumed that platinum hydride was formed on the electrode surface, but it is immaterial for our purposes whether the explanation is hydrogen adsorption or compound formation.

When oxygen was bubbled through a low resistance solution it reacted with and removed the adsorbed hydrogen, leaving an active platinum surface on which hydrochloric acid was adsorbed rapidly. The resistance therefore rose suddenly to a peak value.

In the oxygen atmosphere, platinized platinum was re-oxidized. As the extent of the oxide layer increased, the amount of hydrochloric acid which could remain adsorbed decreased. Its entrance into the solution caused the resistance to fall slowly over a period of several hours. Eventually, the surface became covered with the oxide layer, on which only the normal amount of hydrochloric acid could remain adsorbed. The solution regained its original concentration when all hydrochloric acid in excess of the normal quantity on the electrodes had entered the solution; consequently the final resistance was almost the same as the

¹Hofmann, Ber., 56, 1166 (1923).

standard value.

In conclusion, the hydrogen peak was reached when the rate at which adsorbed hydrochloric acid was being forced into the solution by hydrogen adsorption became equal to the rate at which it was being adsorbed, due to conversion of the electrode oxide layer into platinum. The corresponding oxygen peak was reached when the rate at which adsorbed hydrochloric acid was being removed from the surface due to formation of the oxide layer became equal to the rate at which hydrochloric acid was being adsorbed due to formation of a pure platinum surface (when oxygen removed the previously adsorbed hydrogen).

APPLICATIONS

The original object of this work was to find an accurate conductimetric method of analysis of $\text{HCl-H}_2\text{-AgCl}$ solutions removed from an e.m.f. cell. In the light of the finding, it is believed that any one of the following three methods will be satisfactory:

1. Remove the hydrogen electrode from the e.m.f. cell after the final measurement of e.m.f. Bubble nitrogen, air or oxygen through the solution long enough to remove all hydrogen. Measure the resistance of samples of this solution in a conductance cell with platinized electrodes.

2. Remove the hydrogen electrode from the e.m.f. cell after the final measurement of e.m.f., and measure the resistance of samples of the solution in a conductance cell with unplatinized electrodes. The removal of hydrogen from the solutions should not be necessary if they are measured in a conductance cell with unplatinized electrodes.

3. Immediately after the final measurement of e.m.f., determine the resistance between two platinized or unplatinized electrodes immersed in the solution in the e.m.f. cell. This method is the simplest one of the three. Desorption of all hydrochloric acid from the hydrogen electrode and the conductance electrodes would have occurred during the preliminary hours of hydrogen bubbling; the final e.m.f. measurement would correspond, therefore, to the concentration of hydrochloric acid indicated by the resistance measurement. It might be possible to use the conductance electrodes as hydrogen electrodes.

This work suggests also that care must be exercised in the determination of the pH of solutions with a hydrogen electrode if correct results are to be obtained. Accurate results cannot be expected when a hydrogen electrode is immersed in the first sample, and hydrogen bubbled because there may be a desorption of acid from the electrode which will indicate a pH value lower than the true value. The effect of the so-called "hydrogen error" on the apparent pH of buffer salts has been studied recently by several investigators.¹

In general, it cannot be assumed that the concentration of any dilute solution is known accurately after that solution has come in contact with a platinized surface, unless it is analyzed subsequently.

¹Wolf, Z. Elektrochem., 36, 803 (1930); 37, 619 (1931); Landt, Z. Ver. Dtsch. Zuckerind., 969 (1930); ~~Landt~~, Z. Elektrochem., 38, 12 (1932); Halban and Kortüm, Z. Elektrochem., 39, 288 (1933).

SUMMARY

Abnormal resistances were obtained for very dilute solutions of hydrochloric acid, containing silver chloride and hydrogen, when samples of these solutions were measured in a conductance cell to which they had been transferred from the e.m.f. cell for analysis. It was demonstrated that the erratic resistance behavior required the presence of hydrogen, and that the presence of silver chloride was not essential. When air or nitrogen was bubbled for an hour or two through a dilute hydrochloric acid solution containing hydrogen, in a storage flask, samples of the resulting solution displayed a constant and reproducible resistance when measured in a conductance cell. This resistance was very nearly the same as that of the original dilute hydrochloric acid solution, before hydrogen was bubbled into it in the storage flask.

Characteristic time variations were observed when the resistance of a dilute hydrochloric acid solution containing dissolved hydrogen was measured in a conductance cell. The resistance fell several per cent to a minimum during the first fifteen to thirty minutes in the cell, after which it rose slowly at first, then more rapidly to a peak value several per cent higher than the initial resistance. From the peak the resistance fell slowly for several hours and finally reached a more or less steady value near the initial resistance.

The abnormal resistance effects in a conductance cell were greatest for a given concentration when the resistance was measured between freshly platinized electrodes: they decreased

slowly as the electrodes aged. The per cent of abnormality was much less in a conductance cell with a gray form of platinized electrodes, and was very small in a cell the electrodes of which had been platinized from a platinic chloride solution containing no lead acetate. In a cell with unplatinized electrodes, a constant and reproducible resistance was obtained for HCl-H_2 samples; this resistance was essentially the same as that of the hydrochloric acid solution before hydrogen was bubbled through it in the storage flask.

When hydrogen was bubbled through a dilute hydrochloric acid solution while it was in a conductance cell, the resistance rose several per cent, the actual amount depending on the concentration of the solution, to a maximum, called the hydrogen peak, then fell rapidly to a constant value several per cent lower than the standard resistance of the hydrochloric acid solution which was being employed. After oxygen had been bubbled through the same solution for a few minutes, the resistance rose rapidly to a maximum, called the oxygen peak, several per cent higher than standard. The resistance fell slowly from the maximum for several hours whether the bubbling of oxygen was continued or not, and approached the standard value. Samples were removed from a cell when the resistance was (a) near the hydrogen peak, (b) at a constant low value, and (c) at a subsequent oxygen peak, when oxygen replaced hydrogen in a solution. These samples were analyzed by direct titration of total hydrogen or chloride ion concentrations, or by the measurement of their resistance in a cell with unplatinized electrodes. The resistance measurements in the cell with unplatinized electrodes indicated that the observed changes in resistance in the cell with platinized electrodes corresponded to concentration changes throughout the

bulk of the solution. The titrations demonstrated that the changes in resistance in the cell were due largely to variations in the concentration of hydrochloric acid in the solution.

It was shown, in support of the views of Kolthoff and Kameda, that hydrochloric acid was adsorbed on platinized electrodes in an oxygen atmosphere, and was liberated again when hydrogen was bubbled through the same or a subsequent sample of the solution. Presumably hydrogen was adsorbed on the platinum, forcing hydrochloric acid into the solution. A knowledge of the previous history of an electrode was therefore important; consequently the resistance of each sample which came into contact with the cell electrodes was measured, that is, the cell was not rinsed between samples.

If the hydrochloric acid concentration was not less than 0.01 M, the amount of hydrochloric acid which disappeared, adsorbed on the electrodes, when oxygen was bubbled through one sample nearly all reappeared when hydrogen was bubbled through the subsequent sample until a constant low resistance was attained. This quantitative agreement occurred regardless of changes in the volumes of the samples. A net loss of hydrochloric acid occurred when hydrogen and oxygen were bubbled through alternate samples of a hydrochloric acid solution more dilute than 0.01 M. The per cent loss was greater, the more dilute the solution. The oxidation in the presence of the platinized electrodes of a small amount of hydrochloric acid to chlorine or one of its oxidation products accounted for the observed loss in hydrochloric acid. This oxidation occurred in the samples through which hydrogen was bubbled. In addition, traces of H_2O_2 were detected in some HCl-H_2 samples which had been in contact with platinized electrodes in a conductance cell.

An attempt was made to apply the Freundlich adsorption isotherm to the adsorption of hydrochloric acid on platinized platinum. The equation which was obtained fitted the data approximately. An error was introduced by the oxidation in the cell of a small amount of hydrochloric acid. The ease with which the electrodes adsorbed an amount of hydrochloric acid far in excess of the equilibrium quantity, nearly twice as great at the oxygen peak, introduced another error. The excess hydrochloric acid returned to the solution very slowly, and it was difficult to ascertain when the electrodes held only the equilibrium quantity of hydrochloric acid.

The quantity of hydrochloric acid adsorbed on the particular platinized electrodes which were employed, varied from approximately $6 - 6.5 \times 10^{-6}$ moles in a 0.01 M solution to $2 - 3 \times 10^{-6}$ moles in a 0.001 M solution. Six months later the amount adsorbed on the same electrodes from a 0.001 M solution had decreased to $1.5 - 2 \times 10^{-6}$ moles.

A theory was developed involving the oxidation and subsequent reduction of the platinized electrode surfaces, to explain the occurrence of hydrogen and oxygen resistance peaks.

Suggestions have been made as to desirable changes in the conductimetric method of analysis of HCl-H₂-AgCl solutions from an e.m.f. cell. The results of this investigation have been discussed also in connection with the accurate determination of the pH of solutions by means of a hydrogen electrode.

